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Preparation of $RuSr_2GdCu_2O_8$ Compounds with Enhanced Superconducting Transition Temperature

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The $RuSr_2GdCu_2O_8$ (Ru1212) crystal with the highest superconducting transition temperature $T_{c(end)}$=54.0 K ($T_{c(onset)}$=65.0 K) has been obtained from the nominal composition of Ru:Sr:Gd:Cu=0.9:2.0:1.0:2.1. The prepared compounds are not in a single Ru1212 phase and contain a small amount of Sr_2GdRuO_6 and $SrRuO_3$ impurity phases. Possible correlation between the high-T_c phase and the impurity phase is discussed.

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1. INTRODUCTION

The coexistence of superconductivity and ferromagnetism in the $RuSr_2GdCu_2O_8$ (Ru1212) compound has raised considerable interest[1,2]. The crystal structure of Ru1212 is an analog of $YBa_2Cu_3O_7$ with complete replacement of the Cu-O chains by RuO_6 octahedra. There are many researches of this system, *e.g.*, electrical, magnetic, structural and thermal properties, aiming to elucidate the interplay between superconductivity and magnetism in high-T_c oxides[3–5]. The reported superconducting transition temperature T_c is, however, fairly dispersed ($T_{c(end)}$(zero resistance T_c)=15∼45 K[2,4–6]) and the systematic relation between T_c and the oxygen and ruthenium contents has not been well established. Recently, Klamut *et al.* investigated the superconductivity in the Ru-deficient $Ru_{1-X}Sr_2GdCu_{2+X}O_{8-y}$ compounds sintered under a high oxygen pressure[7] and the onset T_c is significantly enhanced up to $T_{c(onset)}$=72 K for the X=0.3 and 0.4 samples. We fabricated the $RuSr_2GdCu_2O_8$ and $Ru_{1-X}Sr_2GdCu_{2+X}O_8$ compounds under atmospheric pressure using various sintering and annealing temperatures. Under proper conditions, the Ru1212 system was found to achieve zero resistance at as high as 54.0 K.

2. EXPERIMENTAL

$RuSr_2GdCu_2O_8$ samples were prepared from stoichiometric mixtures of RuO_2, $SrCO_3$, Gd_2O_3 and CuO powders. The mixtures were calcined at 950°C for 30 h in N_2 atmosphere, pressed into pellets and then sintered at various sintering temperatures T_s (=1120 ~ 1250°C) for 30 h in flowing O_2. The sintered samples were heat-treated at 1000°C for 168 h in flowing O_2. The Ru deficient $Ru_{1-X}Sr_2GdCu_{2+X}O_8$ compounds (X=0.1, 0.2 and 0.3) were also fabricated under the same conditions. The electrical resistivity $\rho(T)$ was measured by a standard four-terminal method and the magnetization $M(T)$ was measured by a SQUID magnetometer. X-ray diffraction (XRD) data were collected using the CuKα radiation. Rietveld analysis[8] was performed to estimate the lattice parameters (a and c) and the volume fraction ratios of the Ru1212 and other impurity phases.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the temperature dependence of the electrical resistivity $\rho(T)$ of the annealed samples for various T_s. The optimum sintering temperature in this system has been believed to be T_s~1060°C [2,4]. Since our samples fabricated at T_s=1060°C were porous and showed the high resistivity and the low T_c values, we increased T_s up to just below the melting temperature. This procedure resulted in the $T_{c(end)}$ increase with the maximum at $T_{c(end)}$=49.5 K (T_s=1170~1220°C). With further increase of T_s, $T_{c(end)}$ decreased. The absolute value of $\rho(T)$ showed a minimum for T_s=1190°C. The $\rho(T)$ curves are metallic for T_s=1150 ~ 1220°C and show no anomaly at the magnetic ordering temperature T_M (~130 K). Figure 1(b) presents $T_{c(end)}$ of the as-sintered and O_2 annealed samples as a function of T_s. The $T_{c(end)}$ of 49.5 K was obtained only for the O_2 annealed samples ($T_{c(onset)}$=65.0 K). $T_{c(end)}$ increased by about 20 K through annealing. Figure 1(c) shows the magnetization $M(T)$ of the T_s=1190°C sample after the process of zero field cooling (ZFC). The clear Meissner signals are observable for the applied field of up to 50 G. This result is rather surprising because the Meissner signal has been reported to be detectable only below the applied field of a few Gauss[4,7]. T_c determined from M(T) is ~40 K and significantly lower than that determined from $\rho(T)$. M(T) clearly exhibits the sign of magnetic ordering at T_M=130 K.

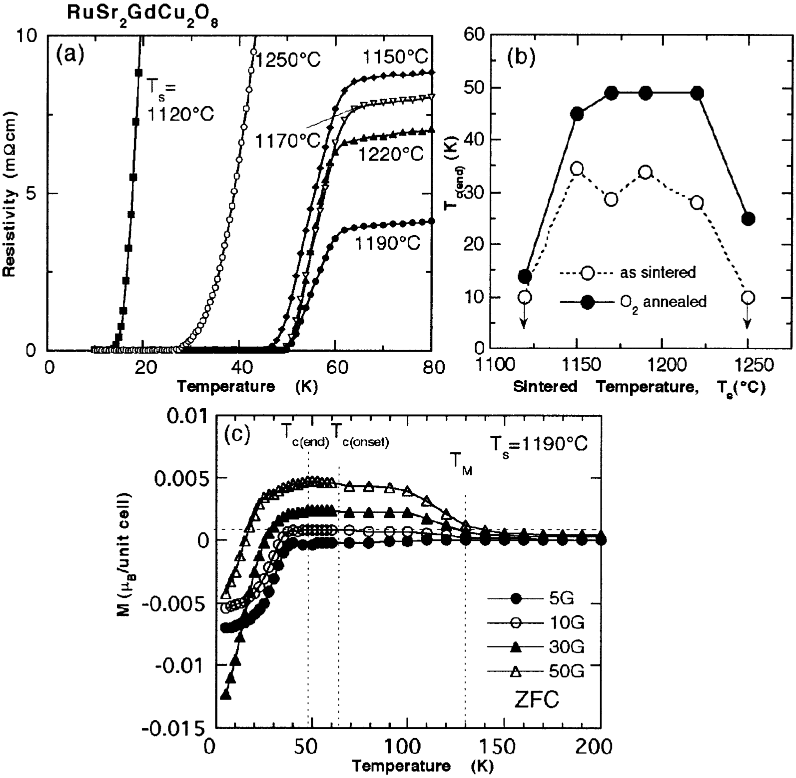

Fig. 1. (a) The temperature dependence of the electrical resistivity $\rho(T)$ of the O_2 annealed samples for various sintering temperatures T_s. (b) $T_{c(end)}$ of the as-sintered and O_2 annealed samples as a function of T_s. (c) $M(T)$ for the T_s=1190°C sample after the process of zero field cooling (ZFC).

The prepared compounds, however, turned out not to be in a single Ru1212 phase and contained a small amount of Sr_2GdRuO_6 (211) and $SrRuO_3$ (113) impurity phases. Figure 2(a) shows the XRD patterns of the samples for various T_s. The diffraction peaks of the 211 and 113 impurity phases are observable besides those of the Ru1212 phase. The impurity phases seem to somewhat increase with increasing T_s. For the T_s=1190°C sample, for example, the volume fractions of the 211 and 113 phases are estimated to be 5.2% and 18.3%, respectively, by the Rietveld analysis, while they are estimated to be 4.7% and 16.3% for T_s=1150°C. The segregation of these Ru-containing impurity phases suggests the formation of a Ru-poor (and Cu-rich) Ru1212 superconducting phase because the sample prepara-

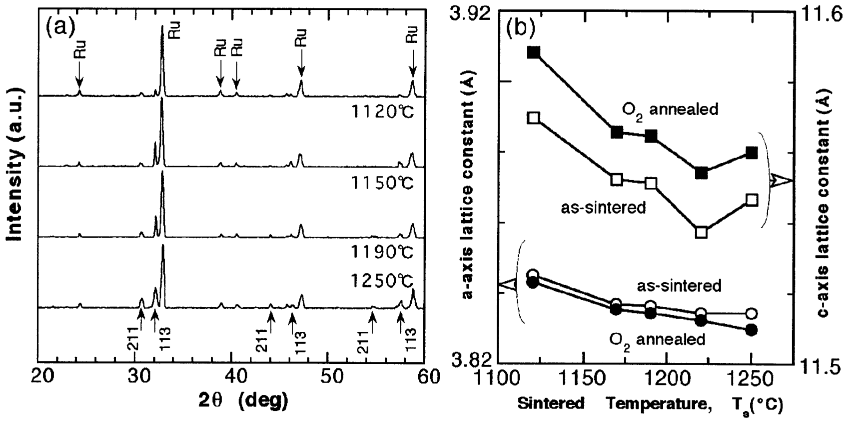

Fig. 2. (a) The XRD patterns of $RuSr_2GdCu_2O_8$ samples for various T_s. In this figure, 'Ru', '211' and '113' show the Ru1212, Sr_2GdRuO_6, and $SrRuO_3$ phases, respectively. (b) The a- and c-axis lattice parameters of the as-sintered and O_2 annealed samples as a function of T_s.

tion started from a stoichiometric mixture of the metallic elements. Figure 2(b) shows the a- and c-axis lattice parameters of the as-sintered and the O_2 annealed samples as a function of T_s. The a- and c-axis lattice parameters decrease with increasing T_s. After the annealing in flowing O_2, the c-axis parameter distinctly increases and the a-axis one slightly decreases. This result implies that the enhancement of $T_{c(end)}$ by the O_2 anneal is related to the c-axis elongation.

Figure 3(a) shows $\rho(T)$ of the O_2 annealed $Ru_{1-X}Sr_2GdCu_{2+X}O_8$ samples as a function of X (T_s=1150°C). For the X=0.1 sample, $T_{c(end)}$ increases to 54.0 K and then decreases for larger X. The ρ values in the normal state are also the smallest for X=0.1. Comparing the $\rho(T)$ curve of the X=0.1 sample ($T_{c(end)}$=54.0 K, $T_{c(onset)}$=65.0 K) with that of the X=0.4 sample of Klamut *et al.*[7] with the highest reported $T_{c(onset)}$ ($T_{c(end)}$=46 K, $T_{c(onset)}$=72 K), the $\rho(T)$ transition curve of the present sample does not show the shoulder-like structure characteristic of their high $T_{c(onset)}$ sample. Figure 3(b) presents the $T_{c(end)}$ and the resistivity at 100 K, ρ(100 K) of the T_s=1150°C and the T_s=1180°C samples as a function of X. The ρ value in the normal state takes a minimum at X=0.1. From the Rietveld analysis of XRD data, it is found that the volume fractions of the impurity phases are reduced for the X=0.1 sample (211: 4.1%, 113: 8.6%), compared with those of the X=0 sample (211: 4.7%, 113: 16.3%). The enhancement of $T_{c(end)}$ for the $Ru_{1-X}Sr_2GdCu_{2+X}O_8$ (X=0.1) sample may be related to the decrease

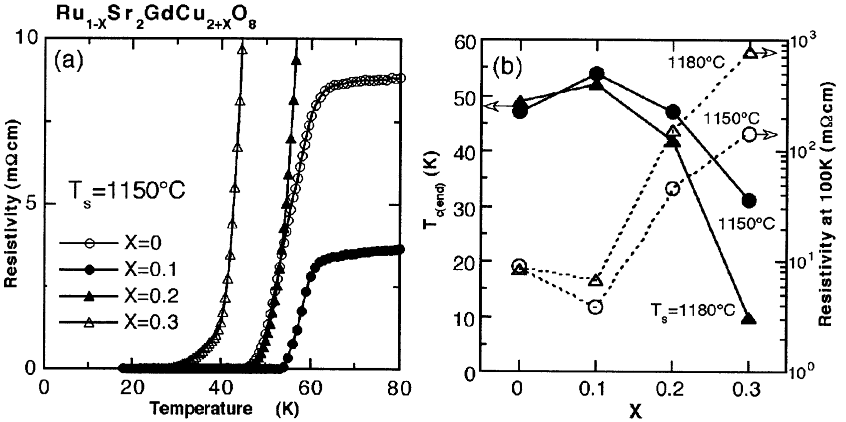

Fig. 3. (a) $\rho(T)$ of the $Ru_{1-X}Sr_2GdCu_{2+X}O_8$ samples. (b) $T_{c(end)}$ and the resistivity at 100 K of the respective samples as a function of X.

of the impurity phases.

In summary, the $RuSr_2GdCu_2O_8$ (Ru1212) compounds have been fabricated by the modified sample preparation processes. By setting the nominal composition at Ru:Sr:Gd:Cu=0.9:2.0:1.0:2.1 (X=0.1), the superconducting transition temperature $T_{c(end)}$=54.0 K (at zero resistivity) was achieved which is the highest reported so far. The higher $T_{c(end)}$ may come from the reduction of the contained Sr_2GdRuO_6 and $SrRuO_3$ impurity phases, compared with those for the X=0 sample ($T_{c(end)}$= 49.5 K).

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